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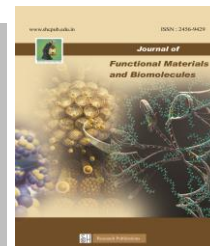
Effect of plasticizer on PVP based polymer electrolyte complexed with 2 – amino benzene sulphonic acid

R. S. Diana Sangeetha[*1]

Abstract

The addition of different organic plasticizers to the Poly vinyl pyrrolidone – 9 mol % 2- Amino benzene sulphonic acid (P2A9) has been found to remarkably affect the conductivity of the polymer electrolyte. The various organic solvent such as poly ethylene glycol (PEG$_{200}$), Diethylene oxide (DEO), IGEPAL, Ethylene carbonate (EC), Propylene carbonate (PC) and Dimethyl formamide (DMF) had been used as a plasticizers. The plasticized polymer electrolyte has been prepared by solution casting technique. The complex impedance measurements carried out using a computer-controlled electrochemical work station (Biologic Science Instrument France Model – SP 300) in the frequency range of 100 Hz - 5MHz with an applied voltage of 100 mV at room temperature and the other electrical characterizations performed were presented and discussed. The electrochemical characterization reveals that the additions of diethylene oxide plasticizer increase the conductivity of P2A9 polymer electrolyte at room temperature.

Keywords: Poly vinyl pyrrolidone, Diethylene oxide, Plasticizer.

1 Introduction

In my previous work, the amino benzene sulphonic acid (ABSA) salt is used as a dopant to enhance the conductivity of PVP, because the sulphonic acid group in ABSA could form an ionically cross linked ionomer networks could promote proton transfer; owing to the strong polarity of the molecule[1]. The PVP complexed with 9 mol% of 2-amino benzoic acid (P2A9) should possess a highest conductivity (8.44x 10^{-6} S/cm) was already reported [2]. The dielectric properties of polymer materials play an important role in applications of electrochemical devices. From the fundamental point of view, dielectric relaxation spectroscopy has been widely used to realize the microscopic dynamical relaxation process in complicated systems. The dielectric properties of polymer electrolyte have been further increased by adding the low dielectric constant solvent, which are going to act as a plasticizer.

The addition of plasticizer has a great importance to increase the conductivity of polymer electrolytes. Plasticizer can help in improving the electrical conductivity of polymer electrolytes in three ways.

(i) By increasing the amorphous content of the polymer electrolytes at all salt concentrations.
(ii) By dissociating the ion aggregates in polymer electrolytes, which are predominant in high salt concentrations.
(iii) By lowering the glass transition temperature and increasing the segmental mobility.

Many researchers have been working in the plasticized polymer electrolytes. They have reported the conductivity values in the range of 10^{-7} to 10^{-3} S/cm at ambient temperature [3-9].

2 Experimental

Poly (vinyl pyrrolidone) (PVP) K$_{90}$ (Sd fine – chem. Limited, India.), 2 – amino benzene sulphonic acid (ABSA) (Tokyo Chemical Industry –Co. Ltd. Japan.), DMF (Merck), Poly Ethylene Glycol$_{200}$ (Merck, Mean MW=190-210), IGEPAL, Diethylene oxide (DEO), Ethylene carbonate (EC) and propylene carbonate (PC) (Sigma – Aldrich) – 99% purity were used as raw materials. Plasticized polymer electrolytes have been prepared with 10 mol% of different plasticizer in PVP complexed with 9 mol% of 2-amino benzene sulphonic acid isomers by solution casting technique using water as solvent. The complex impedance measurements are carried out using a computer-controlled electrochemical work station (Biologic Science Instrument France Model – SP 300) in the frequency range of 100 Hz - 5MHz with an applied voltage of 100 mV at room temperatures.

3 Results and Discussion
3.1 Impedance Analysis:

The ionic conductivity values of the electrolytes are calculated by using the equation:

$$\sigma = d/ R_b A;$$

where, d and A are the thickness and known area of the electrolyte film and R$_b$ is the bulk resistance of the electrolyte film.

Figure 1 shows that the impedance spectra of P2A9 with different plasticiser at room temperature. The nyquist plot has two well-known semi – circular high fre-

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quency and spike in low frequency region. The semicircle at high frequency region indicates the bulk effect of electrolytes and linear region in low frequency is responsible for the effect of blocking electrodes [13].The conductivity of plasticized polymer electrolytes have been calculated and listed in the table 1.
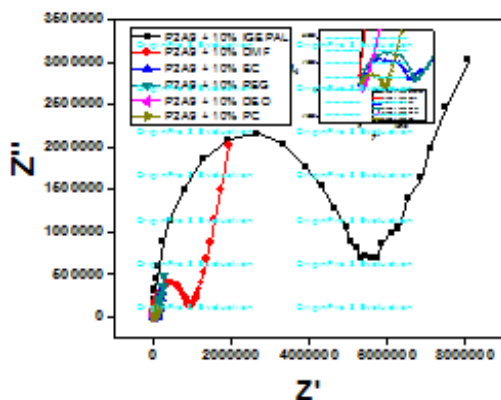

Figure 1: Impedance Plot of P2A9 with different plasticiser at room temperature.

From the figure 2, it infers that the diethylene oxide increase the conductivity value of P2A9 from 10^{-6} to 10^{-5}S/cm. Others are inhibiting the ionic conduction in the P2A9 polymer electrolyte and also it reduces the segmental motion of the polymer chain. It increases the rigidity of the polymer.
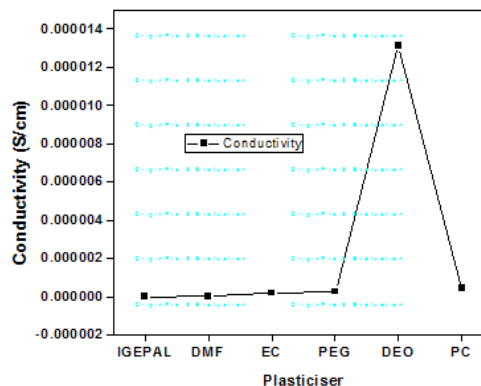

Figure 2: Conductivity of P2A9 with different Plasticizer

Table 1: Conductivity values for P2A9 with different plasticiser

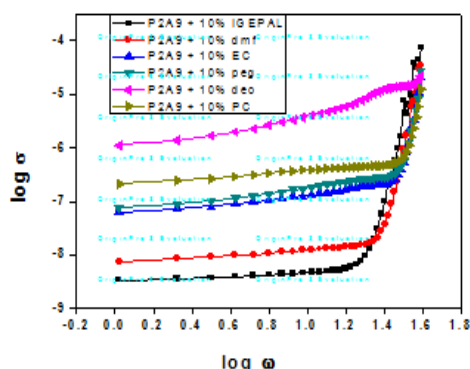| Sample	d (thickness)	Rb	A	$\sigma = d/R_bA$ (S/cm)
P2A9 + 10% IGEPAL	0.0358	5443803	1.4	4.69735 X 10^{-09}
P2A9 + 10% DMF	0.0185	936916.9	1.4	1.4104 X 10^{-08}
P2A9 + 10% EC	0.016775	58532.78	1.4	2.04708 X 10^{-07}
P2A9 + 10% PEG	0.0254	66432.27	1.4	2.73103 X 10^{-07}
P2A9 + 10% DEO	0.030625	1669.457	1.4	1.31031 X 10^{-05}
P2A9 + 10% PC	0.018575	29007.71	1.4	4.57391 X 10^{-07}

3.2 Conductance spectra Analysis

Figure 3: Conductance spectra of P2A9 with different plasticizer at room temperature.

The frequency dependence of conductivity for the entire plasticized polymer electrolytes at room temperature are shown in figure 3. Typical conductance spectra consists of three distinct regions: the low frequency spike describing electrode–electrolyte interfacial phenomena, followed by the frequency independent plateau region connected with the σ_{dc} of the complexed polymer electrolyte and the final high frequency region corresponding to the bulk relaxation phenomena[14]. The low frequency region is not predominant in these system, that means the electrode – electrolyte interfacial effect was reduced due to the addition of plasticizer was found. So that the ionic mobility in the interfacial region is reduces except addition of DEO and thus conductivity decreases. The dc conductivity of the prepared polymer electrolyte has been obtained by extrapolating the plateau region on the log σ axis. The calculated dc conductivity values from the conductance spectra are in good agreement with those obtained from the Cole–Cole plot.

3.3. Dissipation Factor Analysis:

The dielectric power loss is referred to the dissipation factor (D_e) or loss tangent (tan δ) and is given as

$$D_e= \varepsilon''/\varepsilon' = \text{Tan } \delta.$$

where δ is the loss angle.

Figure 4 shows the angular frequency dependence of the tan δ as a function of plasticizer for the P2A9 polymer electrolytes.

The tan δ is found to increase with increasing frequency and attains a maximum value (tan δ $_{max}$) then decreases with further increase of frequency. At low frequencies, the dipoles are able to keep in phase with the change of electric field and hence the power losses are low. As the
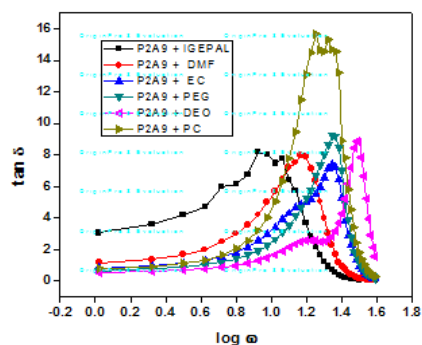
Figure 4: Variation of tan δ with different plasticizer for P2A9 polymer electrolytes at different frequencies.

frequency was increased the dipole reorientation could not be completed in the time available and the dipole become out of phase with the electric field and, hence, the power loss is maximum.

The angular frequency (ω_H) corresponding to tan δ$_{max}$ described by the relation $\omega_p\tau = 1$ and is called 'Hopping frequency'. The relaxation time (τ) of this polymer electrolyte is calculated from the above relation. The table 2 represents the relaxation time for plasticized P2A9 polymer electrolytes system at room temperature. The less relaxation time is observed for PC plasticized with P2A9 polymer.

Table 2: Relaxation time for P2A9 with different plasticizer based polymer electrolytes at room temperature

S.No	Sample	ω_p	Relaxation time = $1/ \omega_p$
1	P2A9 + IGEPAL	8.039323	0.124389
2	P2A9 + DMF	7.975423	0.125385
3	P2A9 + EC	7.282359	0.137318
4	P2A9 + PEG	9.238667	0.108241
5	P2A9 + DEO	8.796286	0.113684
6	P2A9 + PC	15.67777	0.063785

4 Conclusions

Solvent free plasticized PVP complexed with 9 mol% 2- amino benzene sulphonic acid with different plasticizer has been prepared by solution casting method. The conductivity and relaxation time measurements have been determined by using the AC impedance spectroscopy. The impedance spectra analysis shows that the diethylene oxide (DEO) increases the ionic conduction and also increases the segmental motion of the polymer to some extent. The addition of other plasticisers like DMF, PEG, EC, IGEPAL and PC decrease the surface excess charge density at interfacial region, which leads to decrease in ionic conduction and increase the rigidity of the polymer. The low relaxation time has been found by the addition of PC indicates that may be the PC may also act as a good plasticizer.

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